

AQUA Progress report: *Infrared Laboratory Spectroscopy for AIRS, TES and HIRDLS*

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Proposal Summary

The research objectives of this project are to support three **EOS** experiments (**AIRS**, **TES** and **HIRDLS**) by improving the database of air-broadened line shape parameters for water, nitrogen dioxide, methane and carbon monoxide in the 5 to 10 μm spectral region. For the first two species, new laboratory measurements are being obtained while for the last two, new measurements from other studies are being evaluated and written into electronic format for immediate use by the instrument science teams and for future improvements to the **HITRAN** database.

Overview of Activities and Accomplishments

Laboratory absorption spectra have been recorded at high resolution using the McMath-Pierce Fourier transform spectrometers at the National Solar Observatory (AZ). Thus far 36 spectra of water + air and 19 spectra of nitrogen dioxide + air have been obtained using heatable and coolable absorption cells. Gas sample mixtures are held at temperatures ranging from 225 K to 450 K. In April, additional spectra of both species are scheduled to be recorded using the Bruker FTS at the Pacific Northwest National Laboratory (WA) in order to obtain longer path spectra for the water and better resolution data for nitrogen dioxide. Retrieval and modeling software programs at William and Mary and JPL have been revised in order to measure and analyze these data. For the databases, methane and carbon monoxide line shape parameters have been revised for the spectral regions used by **AIRS**, **TES** and **HIRDLS**.

To facilitate communication with these **EOS** science teams, Brown has become an associate member of the **TES** science team and attends their weekly meetings. She also responded to a request from the European **MIPAS** science team to correct some deficiencies in their customized database of spectroscopic parameters. She receives updates about the **AIRS** data via Dr. Mike Gunson. At Langley, Smith, Devi and Benner are in contact with Curtis Rinsland about the needs of **TES**. All investigators on this task work closely with Larry Rothman in order to improve the **HITRAN** compilation.

Review papers for a special issue of Journal of Quantitative Spectroscopy and Radiative Transfer have been submitted to describe the available parameters and future needs for methane and other species. To complete the room temperature database for line shapes of foreign-broadened water at room temperature, measurements of water broadened by oxygen were analyzed; the paper reporting these results is in press in the Journal of Molecular Spectroscopy. New laboratory results of hot and cold temperature air-broadened water will be presented in June 2003 at the 57th Symposium for Molecular Spectroscopy in Columbus, OH, and a paper is in preparation.

Publications:

R. A Toth and L. R. Brown, Oxygen broadening parameters of water vapor: 1212-2136 cm^{-1} , (in press, J. Mol. Spectrosc.).

J.-M Flaud, C. Piccolo, B. Carli, A. Perrin, L. H. Coudert, J.-L. Teffo and L. R. Brown, Molecular line parameters for the **MIPAS** (Michelson Interferometer for Passive Atmospheric Sounding) experiment, (*accepted* for the Atmospheric and Oceanic Optics journal and published in Russian in No. 3, 2003 (the topical issue for ASA-2002). This will later be published in English.

L. R. Brown, D. Chris Benner, J.P. Champion, V.M. Devi, L. Fejard, R.R. Gamache, T. Gabard, J.C. Hilico, B. Lavorel, M. Loete, G. Ch. Mellau, A. Nikitin, A. S. Pine, A. Predoi-Cross, C. P. Rinsland, O. Robert, R. L. Sams, M.A.H. Smith, S. A. Tashkun, and V.I. G. Tyuterev, Methane line parameters in **HITRAN**, accepted for J. Quant. Spectrosc. Rad. Transfer.

L.S. Rothman, A. Barbe, D.C. Benner, L.R. Brown, C. Camy-Peyret, M.R. Carleer, K. Chance, C. Clerbaux, V. Dana, V.M. Devi, A. Fayt, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, K.W. Jucks, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, V. Nemtchinov, D.A. Newnham, A. Perrin, C.P. Rinsland, J. Schroeder, K.M. Smith, M.A.H. Smith, K. Tang, R.A. Toth, J. Vander Auwera, P. Varanasi and K. Yoshino, The **HITRAN** Molecular Spectroscopic Database: Edition of 2000 Including Updates through 2001, *submitted* to J. Quant. Spectrosc. Rad. Transfer.

R. A. Toth, L. R. Brown, M. A. H. Smith, V. Malathy Devi, D. Chris Benner and M. Dulick, Temperature dependence of air-broadened line widths and shifts of H_2O at 6 μm , the 57th International Symposium on Molecular Spectroscopy, the Ohio State University, Columbus, OH, 2003 and a paper in preparation.

Descriptions by molecule

H_2^{16}O : temperature dependence of air-broadened line widths and shifts

Air-broadened half-widths and pressure-induced frequency shifts of water vapor were derived from laboratory spectra recorded in the 5 to 14 μm spectral interval. A heatable cell with an optical path of 4.4 m and a coolable cell of 0.5 m were used. The observations were obtained at gas sample temperatures ranging from 241 to 388 K and covered rotational transitions in the (000)-(000), (010)-(000), and (020)-(010) bands of H_2^{16}O . Width and shift measurements were determined for over 500 lines, and for each line, the linewidth results were analyzed to obtain the exponent, n , which relates the linewidth coefficient at one temperature to that at another temperature. Further, the values of n were fitted to a smoothing function for sets of families of transitions; this permits us to provide good values in the database for transitions that are not directly measured. Overall, the values of n were found to decrease in size with increasing rotational

quantum number, J. The lineshift analysis is not yet complete. However preliminary results reveal a trend suggesting that for a given line, the magnitude of the shift coefficient increases inversely proportional to the temperature representing the measurement. Additional spectra will be taken at longer path in order to obtain the coefficients for the weaker transitions.

NO₂: air-broadened line widths and shifts at room and cold temperatures.

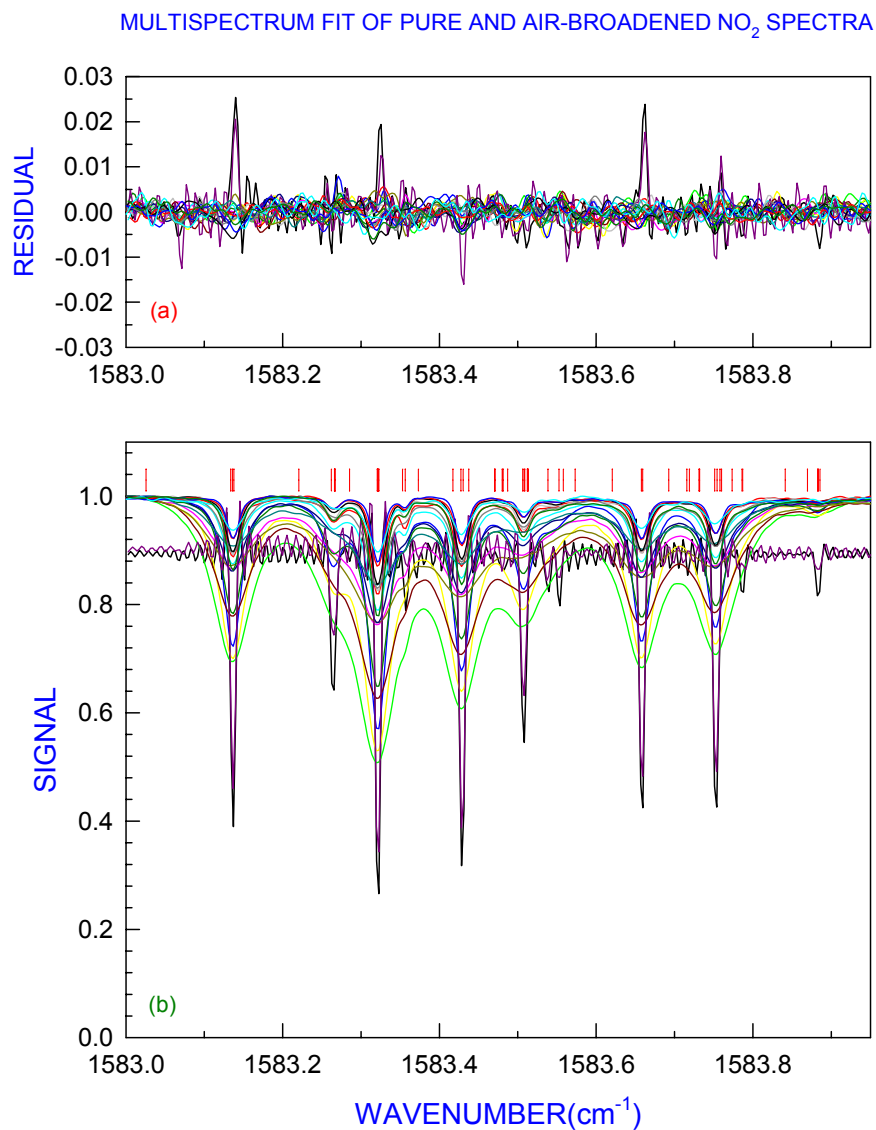
This portion of the task began last November with the acquisition of 21 spectra of NO₂. Spectra were obtained with an instrumental resolution of 0.006 cm⁻¹. Gas samples were in a 50 cm length cell with temperatures varied between 298 K and 219 K. Two scans were obtained using pure samples of NO₂ at low pressures (<0.1 Torr) while the remaining spectra were recorded with lean mixtures (0.035 to 0.12%) of NO₂ in dry air with total sample pressures ranging from 50 to 360 Torr. Calibration of the wavenumber scale of each spectrum was performed relative to the well-determined positions of the ν_2 band water vapor lines.

Initial analysis of select regions of the spectra using a multispectrum nonlinear least squares technique was done. This procedure allows fitting specified spectral regions from all 21 spectra simultaneously so that it reduces the random errors of the retrieved data to a minimum and more reliable line parameters can be determined. The figure on the next page gives an example of this. The narrow features arise in the low pressure pure NO₂ while the broader features appear in the spectra with mixtures of air and NO₂.

The initial input list of line positions and intensities, taken from the Update section on the **HITRAN** website, was found to predict the observed spectrum fairly well. Additional spectra are to be recorded at higher resolution using the FTS at the Pacific Northwest National Laboratory in order to investigate the cause of the small residuals in the plot.

During the initial fittings, we quickly realized that, in order to retrieve the best possible results for NO₂ because of its complex (nuclear spin electronic spin interaction) and crowded spectrum (spin-split components), it would be extremely useful to include some constraints into the fitting technique (such as constraining intensities of two spectral lines in a doublet to be the same or in some known ratio). The multispectrum nonlinear least squares fitting technique of the College of William and Mary group has been revised to allow us to do this sort of analysis.

The new technique is being refined during the month of March. It is anticipated that the needed revisions will be completed before the higher resolution spectra are obtained from PNNL and the final effort to analyze the NO₂ spectra is begun. The retrievals will be performed on all spectra simultaneously.



Twenty-one different spectra of NO₂ [pure NO₂ and air-broadened] are shown. Observed spectra are plotted in the lower panel and the observed minus calculated residuals are shown in the upper panel. A multispectrum fitting procedure is used in fitting the data. However, no constraints are included in making this fit.

The CH₄ database of molecular line parameters

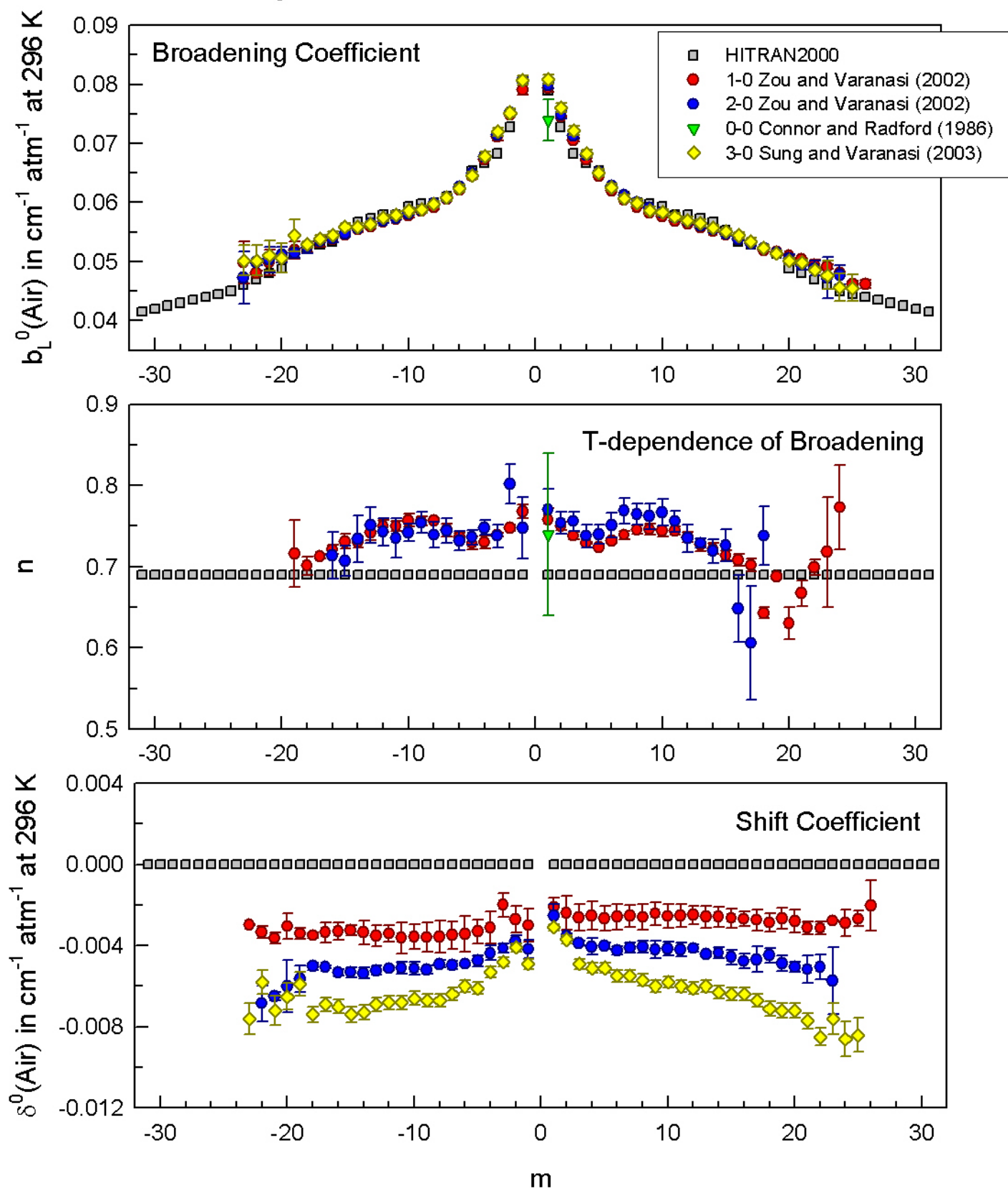
In 2002, the **MIPAS** tropospheric spectra revealed that immediate improvements were needed for the air-broadened line widths and shifts of methane for the intermediate intensity transitions between 5 and 10 μm . In the initial retrievals of their satellite data, the **MIPAS** science team encountered large differences between the observed and synthetic spectra which they identified as being caused by inaccurate line widths and pressure-induced frequency shifts for some of the methane features. Such problems can be expected to impact the **TES** data as well. This situation arises because, while there are tens of thousands of transitions in the methane database, empirical line shape parameters have been obtained for only several hundred of the very strongest transitions. The theoretical models from quantum mechanics do not provide accurate predictions of the coefficients; as a result, the “default” width data available are estimated to be good to only 20%, rather than the 3% required by state-of-the-art remote sensing experiments.

As described in Flaud et al. (see publications above), Brown collected some limited methane results between 6 to 9 μm to form a new interim 2002 version for this region; this was provided to the **MIPAS** team, as well as to **HITRAN** and **GEISA**. Funding from this **AQUA** task was also used to prepare review papers on the methane parameters (Brown et al., Rothman et al.) which discussed the deficiencies in the methane database (as well as other species). The Langley investigators in this task have subsequently undertaken a new study of methane broadened by air in this region (using other funding) to correct more of the line shape parameters.

CO Database of molecular line parameters at 5 μm

The quality of the current **HITRAN** 2000 database was evaluated in light of a number of recent laboratory studies, and a summary of that evaluation has been included in the upcoming journal article describing that database (Rothman et al., 2003). Key problems with the **HITRAN** database were its assignment of a too-low constant value for the temperature-dependence of air-broadening, and its assumption of a value of zero for all pressure-induced CO line shifts by air. A new database was written for the 5 μm region to incorporate improved line broadening and shift parameters. New laboratory results in the 1-0 band (Zou Q, Varanasi P. J Quant Spectrosc Radiat Transfer 2002; 75:63-92). were used for the air-broadening, temperature-dependence of air-broadening, and air-shift parameters. The figure below shows the results available for air-broadening parameters. Self-broadening coefficients in the new line list are based on more than 11 published studies of the fundamental and first two overtone bands of CO. The Langley investigators are planning new measurements of CO spectra in the 5 μm region (using other funding) at Kitt Peak in late 2003. Discussions are continuing with L. Rothman and others regarding an eventual update of the entire CO line list for a future edition of **HITRAN**.

Air-Broadening and Shift Parameters of CO Comparison of Measurements in the Literature



Plans for the remainder of the task

In 2003, we will complete the collection of experimental spectra for water and nitrogen dioxide. The modifications to software will be achieved in the spring so that the retrieval and analyses can proceed during the remainder of the year.

In 2004, manuscripts will be prepared to document our results in the open literature. The individual measurements will be deposited with the journal to be used for future studies, such as the theoretical modeling of line shape parameters. The values will be transmitted to R. Gamache who is performing quantum mechanical modeling of widths and shifts.

We will review all new results from our own work and from others for line widths and shifts of the four molecular species. We will devise appropriate schemes for updating the line shape parameters of unmeasured transitions. We will produce our final versions of updated line parameters for water, nitrogen dioxide, methane and carbon monoxide.

These updated databases will then be validated by Geoff Toon and Bhaswar Sen at JPL by comparison of calculated and observed atmospheric ground-based spectra.

Good communications have been established with the **AIRS** and **TES** science teams, and better contact will be made with **HIRDLS**.

Archival strategy

The resulting databases for water, nitrogen dioxide, methane, and carbon monoxide will be transmitted electronically to the science teams for **AIRS**, **TES** and **HIRDLS**.

The databases will be submitted for inclusion in **HITRAN** and **GEISA**.

Manuscripts describing the databases will be submitted to peer-reviewed journals (such as J. Quant. Spectrosc. Rad. Transfer).